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(54) Closed-cell ethylene polymer stretched films

(57) A substantially closed cell cellular polyolefin stretched film of thickness 150—300 microns and density 550—800 kg/cm³ suitable for wall and ceiling coverings is formed from ether 1) an ethylene homopolymer of density 926 to 930 kg/m³ and defined melt index or 2) a blend of 50—95% by wt. of an ethylene polymer of density 918 to 930 kg/m³ and defined melt index and 50—5% of a crystalline polyolefin, and 0.1—1% by wt. of a gas producing thermally decomparable material having a decomposition temperature of not less than 150°C as the sole blowing agent.

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SPECIFICATION
Cellular polyolefin films

This invention relates to cellular polyolefin films and particularly to such films suitable for use in wall and ceiling coverings.

Numerous proposals have been made for the production of cellular products from thermoplastics polyolefins. However, the commercial production of such cellular products in certain fields has been restricted due to the high cost of production and consequent poor commercial viability.

In the field of cellular polyolefin films suitable for use in wall coverings, it has been proposed that this problem of high production costs, which has been associated with the use of gas producing heat decomposable materials (more usually referred to as chemical blowing agents) as blowing agents, could be overcome by employing two-component physical blowing agents comprising a vaporisable liquid and a gaseous nucleating agent in an extruder injection process. This latter process is cumbersome and requires special equipment and control and there has been a continued need for a more simple yet economic alternative.

British patent specification 1 174 772 is concerned with tapes or ribbons for use in packaging. These tapes or ribbons are formed from foamed olefin polymer. The foamed polyolefin may be made using chemical blowing agents. The properties, in particular ease of handling, of a foamed sheet intended for use as a wall covering will be different from those required from a tape or ribbon intended for tying packages. In particular although the specification states that the variety of polymers can be used there is no disclosure of the specific range of polymers which we have found give particularly good results when used to make wall-coverings.

British patent specification 1 525 224 discloses a stretched polyolefin film of defined characteristics, which is stated to be particularly suitable for packaging purposes. The properties required for a packaging film will not be the same as for a wall-covering. The polymers specifically disclosed in the examples consist of high density polyethylene and the specification indicates a preference for the use of polymer having a high content of high density material. There is no suggestion that advantageous results will be obtained with the particular range of polymers with which our invention is concerned.

We have found that by careful selection of the polyolefin composition, it is possible to produce, simply and economically, substantially closed cell cellular polyolefin stretched films suitable for use in wall and ceiling coverings using a gas producing heat decomposable material as sole blowing agent. We have also found that our selection of polyolefin composition makes possible the production of such films having improved mechanical properties over known commercially available cellular polyolefin wall covering materials while avoiding undesirable crispness in the products. In particular, films having greater tear strength in the machine direction and greater resistance to cold stretching can be produced, the latter being particularly relevant to the ease of pattern register when hanging such wall coverings.

Accordingly, the present invention provides a substantially closed cell cellular polyolefin stretched film having a density in the range 550 to 800 kg/m^3 and thickness in the range 150 to 300 microns suitable for use in wall and ceiling coverings which is formed from:

1) either A — an ethylene homopolymer having a density of 926 to 930 kg/m^3 and melt index of 0.5 to 1.3 g/10 mins,

or B — a blend of 50 to 95% by weight of an ethylene homo- or copolymer of density 918 to 930 kg/m^3 and melt index 0.1 to 2.0 g/10 min and correspondingly 50 to 5% of a crystalline polyolefin, and

2) 0.1 to 1% by weight on the total weight of polymer of a gas producing thermally decomposable material having a decomposition temperature not less than 150°C as sole blowing agent.

By "substantially closed cell" we mean throughout this specification that at least the cells in the body of the film are not interconnecting and by this definition we do not mean to exclude films having one or both major surfaces exhibiting ruptured cells.

The cells of a film of this invention are preferably substantially disc-shaped, and more preferably such that the ratio of machine direction to transverse direction dimensions are from 1.5:1 to 1:1.5, the discs, by definition each having a thickness, measured in the direction of the film thickness, small in relation to the machine or transverse direction dimensions.

The density of a film of this invention is determined from the weight of unit area of film and its micrometer-measured thickness.

The ethylene homopolymer of component A preferably has a density within the range 926 to 928 kg/m^3 and a melt flow index of 0.7 to 1.1/10 min (BS 2782 method 720A Condition 4).

The ethylene homo- or copolymer of component B may be any thermoplastic polymer containing up to 10% by weight preferably up to 5% by weight of comonomer. Examples of such comonomers are vinyl acetate, ethyl acrylate and butyl acrylate, butene, hexene, and octene. When this polymer comprises a linear low density polymer of ethylene the crystalline polyolefin of component B may also comprise the same or a similar polymer. Thus B may be a single linear low density polyethylene. It is preferred that this ethylene homo- or copolymer has a density of 918 to 922 kg/m^3 in particular 920 kg/m^3 and a melt flow index of 0.3 or below.

By crystalline polyolefin we mean throughout this specification a polyolefin having a crystallinity of at least 60% at room temperature. They may be homopolymers or copolymers of alpha-olefins or blends thereof. Polymers of propylene and/or ethylene are preferred. Particularly preferred are the high density polyethylenes of density above 944 kg/m^3 and melt flow index up to 6 g/10 min (BS 2782 method 720A Condition 4). More particularly preferred are high density ethylene homopolymers of density 0.956 to 0.958 kg/m^3 and of melt flow index 0.45 to 0.9 g/10 min.

Suitable gas producing thermally decomposable materials (blowing agents) for use in the production of films in accordance with the present invention can be readily selected by those skilled in the production of polyolefin foams. The temperature at which the blowing agent thermally decomposes to release gas must be above the softening temperature of the polymer A or B used to make the film and in any case must be above 150°C. The man skilled in the production of polyethylene foams will know that it is most desirable to avoid the use of blowing agents which decompose to release gas at temperatures at which substantial degradation of the polymer used to make the film occurs.

Preferred blowing agents are those that are solid at room temperature since they are then easily incorporated into the polymers. Blowing agents that on decomposition produce large volumes of gas per volume of blowing agent are preferred for example azodicarbonamide, p,p'-oxy-bis-(benzene sulphonylhydrazide) and trihydrazino-sym-triazine which have decomposition temperatures in the range 190 to 230°C, 150 to 160°C and 235 to 280°C respectively.

Commercially available forms of these blowing agents are sold under the Registered Trade Marks "Genitron AC", "Genitron OB" and "Genitron THT".

The blowing agent may comprise a single compound or a mixture of compounds. For example, a mixture of azodicarbonamide with a minor amount by weight of tri-hydrazino-sym-triazine may be used. The relative proportions of the two components may be, for example, from 60:1 to 1.01:1 but preferably 6:1 to 3:1 (weight ratio).

The amount of blowing agent employed should be in the range 0.1 to 1% by weight based on the total weight of polymer and preferably in the range 0.3 to 0.7%.

The composition comprising polymer and blowing agent may contain other additives such as organic and/or inorganic fillers, pigments, lubricants, antistatic agents, antioxidants, nucleating agents.

Examples of fillers and pigments which may be used are calcium carbonate and titanium dioxide, which may be present in a total amount of up to 30%, e.g. up to 20% on the total weight of polymer. An example of a lubricant is erucamide which may be in an amount for example corresponding to 0.001 to 1%. An example of a suitable antioxidant is di-butyl-p-cresol. There is a wide variety of finely divided solids which may be used as nucleating agents. These are generally of particle size less than 1 micron and may be incorporated in amounts of, for example, 0.01 to 2%. These percentages are based on the total weight of the polymer.

The polymer and the blowing agent, and the components of the blend B (when B is used), as well as any other desired additives, may be blended together by any of the blending techniques used in the art. For example, blending may be effected on a variety of apparatus including multiroll mills, screw mills, compounding extruders and Banbury mixers, or dissolved in mutual or compatible solvents. Thus, the blending may be effected in a Banbury mixer or continuous extruder followed by a two-roll milling operation to complete the mixing before sheeting and dicing. This technique may be used to prepare a blowing agent masterbatch of course, as is well known in the art, for subsequent blending with complementary components of the composition in an extruder employed for the production of the cellular polyolefin film. Alternatively, for example, the polymer in particulate form may be dust-coated with the blowing agent and fed directly to the said extruder.

The substantially closed cell cellular polyolefin stretched films of this invention may be produced by subjecting the compositions as specified above to conventional flat sheet extrusion and stretching operations or preferably to a blown-film extrusion process applying well known control techniques to obtain the required structure. To this end, we have found that the selected polyolefin composition facilitates the production of stretched films within the specified thickness range while avoiding rupture of the film or substantial rupture of the cells of the cellular structure. The degree of stretching employed will be within the range 1.1:1 to 10:1 in at least one of two principal directions, namely the machine direction and the transverse direction. More usually the degree of stretching employed will be in the range 1.1:1 to 4:1 in each direction. The position within this range at which optimum results can be achieved given polymer composition and conditions of temperature can easily be determined by the persons skilled in making polyolefin foams.

The films of this invention may be subjected to surface treatment, such as chemical oxidation or electrical discharge treatment, to improve the bonding of printing inks and/or adhesives thereto.

The present invention also includes wall or ceiling coverings prepared from the films of the present invention. These coverings may be provided with decorations applied by any of the known techniques by which patterns etc may be applied to wall coverings. The wall coverings of the present invention may be the type in which an adhesive layer is applied during manufacture, making unnecessary any subsequent application of adhesive by the user.

The invention will now be illustrated by the following Examples but which should not be interpreted as limiting the scope thereof. All parts are parts by weight.

EXAMPLE 1

A mixture of 77 parts low density polyethylene (MFI at 190°C using a weight of 2.16 kg was 0.3 and density 920 kg/m³), was blended with 15 parts of high density polyethylene (MFI at 190°C was 0.7, density 956.0 kg/m³), 7.5 parts of titanium dioxide and 0.5 parts of azodicarbonamide blowing agent. The high density polyethylene has a crystallinity well above 60% at room temperature.

The mixture was fed to a $2\frac{1}{2}$" (64 mm) screw extruder with a length to diameter ratio of 20:1. The compression ratio of the extruder screw was 4:1. The resultant mixture was extruded at a temperature of 180°C through a 150 mm diameter annular die set at 0.8 mm gap with foaming occuring a short distance beyond the die lips. The foamed extrudate was blown into a bubble of 300 mm diameter which was collapsed and hauled off by rotating nip rollers at a peripheral speed 4 times that of the linear extrusion speed. The substantially closed cell cellular film thus produced had a thickness of 220 microns and a specific gravity of 0.61.

The cells in the film produced were disc-shaped, each having a dimension in the direction of thickness of the film of from 20 to 30 microns, with the machine and transverse direction dimensions of the discs varying from 410 μm 325 μm respectively for the larger cells to 175 μm in each direction for the smaller cells.

The following results of physical tests carried out on the film and on a currently commercially available cellular polyolefin wall covering material illustrate the improved physical properties of the film produced:

	Example 1 Film Material	Current Commercial Film Material
Secant Modulus (MN/m²)		
Machine Direction (MD)	132	88
Transverse Direction (TD)	112	10
Tear Propagation Strength (gm)		
MD	165	82
TD	216	109
Thickness (microns)	220	350

EXAMPLE 2

A polyethylene foam film was produced by the film blowing process as in Example 1.

The film was formed from a blend of the following composition.

	Percent weight
LDPE	64.48
HDPE	15.0
TiO_2	6.0
$CaCO_3$	14.0
azodicarbonamide	0.4
antistatic agent	0.12

The LDPE was a low density polyethylene made by high pressure polymerisation with MFI of 0.4 and density 921 kg/m³.

The HDPE was a high density polyethylene with a MFI of 0.7 and a density of 957 kg/m³. It had a crystallinity of well above 60% at room temperature. The thickness of the cellular film produced was 230 μm and the density was 610 kg/m³. The film was subjected to a corona discharge treatment on both surfaces to increase its receptivity to printing inks and adhesives. The level of treatment used was such as to give a test result of 42 dynes/cm on the side for printing and 35 dynes/cm on the side to which adhesive was to be applied when tested according to ASTM 2578—677 a test widely used in the polyethylene film industry.

The cellular film produced had an attractive matt appearance and had mechanical properties, including handlability, which made it suitable for use as a wall-covering.

EXAMPLE 3

One hundred parts by weight of an ethylene homopolymer (density 928 kg/m³ and MFI of 190°C (using a weight of 216 kg) of 1.0 g/10 min) were blended with 7.5 parts by weight TiO_2 and 0.5 parts by azodicarbonamide blowing agent in a Banbury mixer and the blend was then sheeted on a two roll mill, cooled, and diced. The compound produced as above was fed to the extruder used in Example 1 and extruded under the same conditions to produce a substantially closed cell cellular film of thickness 210 μm and specific gravity 0.56. 1 cellular film was then corona discharge treated on both sides as in Example 2.

The product handled well as a wall-covering material.

CLAIMS

1. A substantially closed cell (as hereinbefore defined) cellular polyolefin stretched film having a density in the range 550 to 800 kg/m³ and thickness in the range 150 to 300 microns suitable for use in wall and ceiling coverings which is formed from
1) either A — an ethylene homopolymer having a density of 926 to 930 kg/m³ and melt index of 0.5 to 1.3 g/10 mins,
or B — a blend of 50 to 95% by weight of an ethylene homo- or copolymer of density 918 to 930 kg/m³ and melt index 0.1 to 2.0 g/10 min and correspondingly 50 to 5% of a crystalline polyolefin, and
2) 0.1 to 1% by weight on the total weight of polymer of a gas producing thermally decomposable material having a decomposition temperature not less than 150°C as sole blowing agent.

2. A film as claimed in Claim 1 wherein the cells of the film are substantially disc-shaped.

3. A film as claimed in Claim 2 wherein the ratio of cell dimensions machine direction to transverse direction is from 1.5:1 to 1:1.5.

4. A film as claimed in any one of the preceding claims wherein the ethylene homo- or co- polymer of B has a density of 918 to 922 kg/m³.

5. A film as claimed in any one of the preceding claims wherein the melt flow index of the ethylene homo- or copolymer of B is 0.3 or below.

6. A film as claimed in any one of the preceding claims wherein the ethylene copolymer of B contains up to 5% by weight comonomer.

7. A film as claimed in any one of the preceding claims wherein the crystalline polyolefin is a polymer of propylene and/or ethylene.

8. A film as claimed in Claim 7 wherein the crystalline polyolefin is a high density polyethylene of density greater than 944 kg/m³.

9. A film as claimed in Claim 8 wherein the high density polyethylene is a homopolymer of density 956 to 958 kg/m³.

10. A film as claimed in Claim 8 or 9 wherein the high density polyethylene is a homopolymer which has a melt index in the range 0.45 to 0.9 g/10 min.

11. A film as claimed in any one of Claims 1, 2 and 3 wherein the polymer of A has a density within the range 926 to 928 kg/m³ and a melt flow index of 0.7 to 1.1 g/10 min.

12. A film as claimed in any one of the preceding claims wherein the blowing agent comprises a thermally decomposable material which is a solid at room temperature.

13. A film as claimed in Claim 12 wherein the blowing agent is azodicarbonamide, p,p'-oxy-bis (benzene sulphonylhydrazide), trihydrazino-sym-triazine or a mixture of two or more of these compounds.

14. A film as claimed in Claim 13 wherein the blowing agent comprises a mixture of azodicarbonamide and tri-hydrazino-sym-triazine in a weight ratio in the range 6:1 to 1.01:1.

15. A film as claimed in Claim 14 wherein the weight ratio is within the range 6:1 to 3:1.

16. A film as claimed in any one of the preceding claims wherein the amount of blowing agent employed is 0.3 to 0.7% by weight based on the total weight of polymer.

17. A film as claimed in any one of the preceding claims which contains a filler and/or pigment.

18. A film as claimed in Claim 17 wherein the amount of filler and/or pigment is up to 30% by weight on the total weight of polymer.

19. A film as claimed in any one of the preceding claims which is produced employing a blown-film extrusion process.

20. A film as claimed in any one of the precding claims which has been subjected to surface treatment to improve the bonding or printing inks and/or adhesives thereto.

21. A wall or ceiling covering material comprising a substantially closed cell cellular polyolefin stretched film as claimed in any one of the preceding claims.

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